

# INVESTIGATION OF THE CURING VARIABLES OF ASPHALT-RUBBER BINDER

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## INTRODUCTION

Currently, the paving industry utilizes a curing time of 1 hour at 177°C (350°F) for producing asphalt-rubber binder (1). Billiter et al. (2) showed that at these curing conditions, 1 hour at 177°C (350°F), adding rubber to asphalt was beneficial, with the rubber improving the low-temperature creep stiffness at (-15°C (5°F)), the temperature susceptibility in the 0°C-90°C (32°F-194°F) temperature region, increasing  $G^*$  and  $\eta^*$  at 60°C (140°F) and 1.0 rad/sec, and decreasing  $\delta$  at 60°C (140°F) and 1.0 rad/sec. On the other hand, Billiter et al. (2) showed that the addition of rubber was also detrimental, in that the viscosity increased significantly in the compaction temperature region of 149°C-193°C (300°F-380°F). This increased viscosity can cause compaction problems, with Allison (3) reporting that engineers blamed the compaction problems of asphalt-rubber on undissolved crumb rubber, which they believed had no beneficial effect. Additionally, the engineers reported that improper compaction led to early road failure. High compaction viscosities also led to high air void content for dense-graded mixes (4), which is detrimental since Linden et al. (5) reported a correlation between air voids and performance.

Engineers could solve these problems by producing an asphalt-rubber binder with a non-detrimental compaction viscosity. If Allison (3) is correct, then eliminating undissolved rubber from asphalt-rubber binder would help produce such a binder. Apparently, eliminating undissolved rubber is possible, since Billiter et al. (2), Franta (6), and Zanzotto and Kennepohl (7) have reported that rubber devulcanizes and depolymerizes during the application of high shear and high temperature in the presence of asphalt. Obviously, the production of such an asphalt-rubber binder will require a study of the variables of curing time, curing temperature, and the type and amount of mechanical energy. This work investigates these variables in an attempt to produce such an asphalt-rubber binder.

## MATERIALS

Three asphalts were used in this study. Asphalt #1, an AC-10, and Asphalt #2, an AC-5, were acquired from refineries in Texas. Asphalt #3, an AC-10, was produced in the laboratory by blending a commercially available asphalt and a commercially available recycling agent. The asphalt comprised 78% by weight of Asphalt #3 and had a viscosity of 40,710 poise at 60°C (140°F). The recycling agent comprised 22% by weight of Asphalt #3 and had a viscosity of 5.5 poise at 60°C (140°F). Asphalt #3 was produced to study the effect of adding a light aromatic fraction to an asphalt.

Minus 10 and minus 40 mesh rubber were acquired from Granular Products, also known as Tire Gator (TG), located in Mexia, Texas. Additionally, minus 10, 40, and 80 mesh rubber were acquired from Rouse (RS) Rubber located in Vicksburg, Mississippi.

## EXPERIMENTAL METHODS

The bending beam rheometer, dynamic shear rheometer, Brookfield rotational viscometer, Fourier transform infrared spectrometer, and size exclusion chromatograph that were in this study are described in Billiter et al. (2).

### Mixing Apparatus

To produce the asphalt-rubber binders, asphalts and rubbers were 'cured' or mixed at high temperatures (177, 191, or 204°C (350, 375, or 400°F)). Curing is the application of heat and mixing to an asphalt and crumb rubber mixture in which the rubber may be swelled, disintegrated, dissolved, and/or reduced in molecular size. The curing process, as carried out in this laboratory, involved mixing at high temperatures with a 5.1 cm (2") diameter blade driven at 500 rpm or 1550 rpm by a variable speed motor. The blends were cured in 1 gallon paint cans under a nitrogen blanket to prevent the binder from oxidizing.

### Rubber Dissolution Test

The extent to which the rubber had dissolved into the asphalt was determined with the following gravimetric procedure. The analysis was performed using a pre-weighed 0.45  $\mu$ m syringe filter. A 0.2 gram asphalt-rubber sample was dissolved in 10 ml of THF. The asphalt-rubber/THF solution was sonicated for 30 minutes. The solution was then strained through the syringe filter. The filter was heated in a vacuum oven at 100°C (212°F) for 3 hours, removed from the oven and placed at ambient conditions for 24 hours, and finally weighed. The difference between the final filter weight and the initial filter weight is the weight of the rubber that did not dissolve into the asphalt. This weight, the initial sample size weight, and percent rubber content of the initial sample were used to determine the amount of rubber that dissolved into the asphalt.

## EXPERIMENTAL DESIGN

Table 1 shows combinations of temperature, mixer speed, weight percent rubber, rubber mesh size, rubber source, and asphalt used in these sets of experiments. The total curing time was 48 hours for the blends cured at 500 rpm, with samples being taken at 3, 6, 12, 24, 36, and 48 hours. For the 1550 rpm blends, the total curing time was 3 hours, with samples being taken at 1, 2, and 3 hours. Experimental Plan (EP) #1, EP #2, and EP #3 were done to study the variable of curing time. EP #3 was done to study the variable of curing temperature and EP #2 was done to study the variable of mixing power, the authors assuming power is approximately proportional to the square of the blending speed. The asphalt rubber products were evaluated in terms of high-temperature viscosities ( $>121^{\circ}\text{C}$  ( $>250^{\circ}\text{F}$ )), intermediate-temperature rheological properties ( $0^{\circ}\text{C}$  -  $90^{\circ}\text{C}$ , ( $32^{\circ}\text{F}$  -  $194^{\circ}\text{F}$ )), low-temperature creep stiffness at  $-15^{\circ}\text{C}$  ( $5^{\circ}\text{F}$ ), rubber dissolution, molecular weight distribution, and Fourier Transform Infrared Spectrometer (FTIR).

## RESULTS AND DISCUSSION

As discussed in the introduction, previous results in the literature suggest that the dissolution of rubber during the curing process should lead to better binder properties. Consequently, the primary objective of this research was to study the effect of various curing variables on the dissolution of rubber. Specifically, the curing variables of curing time, curing temperature, and rate of mixing are of greatest interest, with the results of the variables of asphalt type, rubber content, rubber mesh size, and rubber source also being presented.

Each figure focuses on a particular variable. If a graph is referenced, at least one example of the comparison being made will be presented.

### Experimental Plan #1

#### Percent Rubber and Mesh Size

For the asphalts studied, the addition of rubber was positive for the low- and intermediate-temperature properties of a binder; the higher the rubber content, within the range studied, the better the results. For a given mesh size, the 10% rubber level lowered the creep stiffness, and therefore improved the elasticity, more than the 5% rubber level, Figure 1. Obviously, the benefits of the elastic additive were more pronounced at the higher concentration levels, thus producing a more flexible binder. Furthermore, the smaller rubber particles were slightly better at improving low-temperature properties, Figure 1. It is theorized that the smaller rubber particles are better able to interact because of their greater surface area per unit mass. The  $60^{\circ}\text{C}$  complex viscosities were higher for the 10% blends and for the larger rubber particles, Figure 2, thereby producing a binder more resistant to rutting. The increase in complex viscosity is probably more of a particle effect than a surface area effect, thus explaining the larger particles' enhanced performance. In the intermediate temperature region, the temperature susceptibility was lower, and therefore better, for the 10% blends and for the smaller rubber particles, Figure 3. In this work the temperature susceptibility is defined in terms of the Andrade equation (8),  $\ln(\eta) = \text{Constant} - E_a/RT$ , in which  $E_a$  is a viscosity activation energy and is a measure of temperature susceptibility. Adding rubber was detrimental to the high-temperature viscosity of an asphalt. The high-temperature viscosity was higher for the 10% blends and the larger particles, Figure 4.

All binder properties were a function of curing time. Although creep stiffness did not improve substantially with curing time, there was always a slight improvement in creep stiffness with curing time, Figure 1. The  $60^{\circ}\text{C}$  complex viscosity increased with curing time, Figure 2. The high-temperature viscosity decreased with curing time, which is desirable, Figure 4. This phenomenon can be explained qualitatively by imaging the rubber particles as rigid spheres and applying an equation derived by Einstein for the viscosity of a dilute suspension of rigid spheres:  $\eta = \eta_s(1 + 2.5\phi)$ , where  $\eta$  is the viscosity of the solution,  $\eta_s$  is the viscosity of the solvent, and  $\phi$  the volume fraction of spheres (9). Obviously, the higher the percent rubber the higher the effective  $\phi$  and thus, the higher the viscosity. Furthermore, the significant decrease in high-temperature viscosity with curing time has to be caused by the rubber particles being reduced in size, thus lowering the effective  $\phi$ , because the viscosity of the asphalt,  $\eta_s$ , is definitely increasing as the particles are devulcanized and depolymerized into the asphalt phase of the solution.

The improvements with curing time in the low- and intermediate-temperature properties, as well as the reduction of high-temperature viscosity, are most certainly explained by the rubber devulcanizing and depolymerizing during the curing process. As noted earlier, the devulcanizing and depolymerizing of rubber during the curing process has been discussed by Billiter et al. (2) and Zanzotto and Kennepohl (7), with support from Franta (6). This phenomenon is represented in Figure 5, a GPC chromatograph of the data of an Asphalt #1 blend as measured by an intrinsic viscosity detector. Figure 5 shows that with curing time there is mass transfer into the asphalt phase. The growth of the peak in the 20 to 25 minute retention time region represents the flux of devulcanized and depolymerized rubber into the asphalt phase of the binder. The molecular weight distribution in this region varies from approximately 190,000 at a retention time of 20.63 minutes to 5,970 at a retention time of 24.37 minutes. Please note that the dissolved rubber molecules represented by the data in Figure 5 are smaller than  $0.45\ \mu\text{m}$  ( $0.45\ \mu\text{m}$ ,  $4500\text{\AA}$ ), since each sample was prepared for GPC injection with a filter that had a pore membrane size of  $0.45\ \mu\text{m}$ . In fact they are generally smaller than  $1000\text{\AA}$ , the pore size of the largest GPC column, as the

chromatograms show little indication of exclusion. The particles are most certainly being devulcanized and depolymerized since they are being reduced from a size of 400-2000 microns to smaller than 1000Å during the curing process.

#### **Comparison of Asphalt Type**

The interaction of the rubber and the base asphalt was very much dependent upon the asphalt composition. Asphalt #3, produced by combining a highly asphaltenic 40,000 poise asphalt with a lower molecular weight 5.5 poise recycling agent, initially interacted with the rubber much better than the other asphalts. This interaction is most certainly explained by the presence of the lower molecular weight recycling agent, which could have just as easily been called a rubber extending oil since such oils are used in the rubber processing industry. Asphalt #3 was able to dissolve much more rubber with curing time, Figure 6. Apparently, the light aromatics of Asphalt #3 are able to interact with the rubber at a much faster rate than the other asphalts, and thus improve the binder properties faster. Similarly, the increase in the 60°C complex viscosity, Figure 2, and the initial improvement in temperature susceptibility, Figure 3, were much greater for Asphalt #3. Although the temperature susceptibility of Asphalt #3 did not continue to improve with time as fast as the other asphalts, the initial improvement offsets this.

The low-temperature performance of Asphalt #3 without rubber, which had a creep stiffness of 377 MPa, was much worse than either Asphalt #1, 208 MPa, or Asphalt #2, 101 MPa. Apparently, not enough of the light aromatics are present to sufficiently peptize the substantial amount of larger molecular weight material present in Asphalt #3. However, with the addition of rubber, the low-temperature properties of Asphalt #3 improved more than the other asphalts, Figure 1. Once again, the other asphalts improve with curing time at a faster rate than Asphalt #3, but the initial decrease in creep stiffness more than offsets this.

At the other end of the temperature scale, the high-temperature viscosity was also very dependent on both asphalt type and curing time. The high-temperature viscosity of Asphalt #1 blends was the most dependent on curing time, Figure 4.

#### **Comparison of Tire Gator and Rouse**

Ground rubbers from two sources were used in this curing study. Rouse rubber was perhaps slightly better at improving the creep stiffness, Figure 1, and 60°C complex viscosity, Figure 2, of Asphalt #1. Sieve analysis showed that for a given mesh size, the size gradation of Rouse rubber was finer than Tire Gator rubber, and thus with more surface area per unit mass, reacted more rapidly, Figure 6. Please note that initially the Rouse -10 mesh particles dissolved faster than even the Tire Gator -40 mesh particles. At high-temperatures the Rouse rubber particles were less detrimental to the viscosity of Asphalt #1, Figure 4. Once again, the Rouse -10 mesh particles are initially better for the binder property than even the Tire Gator -40 particles.

The relative performance of Tire Gator and Rouse rubber was somewhat asphalt dependent. Like Asphalt #1, Asphalt #2 was better able to dissolve the Rouse Rubber, Figure 6. As expected, the creep stiffness, Figure 1, and the temperature susceptibility were better for the Rouse blends. On the other hand, the Rouse rubber was not better for the high-temperature viscosity and the Tire Gator blends actually have a higher 60°C complex viscosity than the Rouse blends, Figure 2. This oddity can most likely be explained by the mesh size, but one of the crumb rubbers may contain more natural than synthetic rubber and be better able to interact with an asphalt of a certain composition.

#### **Experimental Plan #2**

Utilizing a higher shear rate significantly increased the interaction of the rubber and the asphalt. Figure 6 shows that as much crumb rubber dissolves in 2-3 hours utilizing a mixing speed of 1550 rpm as dissolves in 48 hours utilizing a mixing speed of 500 rpm. This strongly indicates that the devulcanization and depolymerization of crumb rubber during the curing process is a mass transfer limited process, with the increased dispersion of the higher mixing speed allowing improved swelling of the rubber and therefore, increased interaction between the asphalt and rubber. As with previous results, the flux of rubber into the asphalt phase improved the low-, intermediate, and high-temperature rheological properties of a binder. Thus, curing at a higher shear rate for a shorter period of time produced similar binder properties as curing the same binder at lower shear for a much longer period of time. In fact, corresponding roughly to the power input it is estimated that increasing the mixing speed three fold, decreases the required curing time nine fold.

#### **Experimental Plan #3**

Increasing the curing temperature significantly increased the interaction between the crumb rubber and the asphalt. Figure 6 shows that the higher the curing temperature the higher the amount of rubber dissolving. Some of the increased interaction can be explained by the lower asphalt viscosity at the higher temperatures causing increased mass transfer between the asphalt and rubber. However, the majority of the increased interaction is probably due to the rubber-asphalt reaction, like any chemical reaction, being very dependent upon temperature. The rubber-asphalt reaction is one of devulcanization and depolymerization in which breaking of the cross-linking network and shortening of the main chains takes place (6). As before, all rheological properties improved with increased rubber dissolution.

## CONCLUSIONS

These results are a powerful indicator that the 1 hour curing time at 177°C (350°F) and relatively low shear, used in the field, are not optimal. On the other hand, the extended curing times utilized in this study would not be agreeable with field personnel. However, the results of this study strongly imply that increasing curing temperature and shear rate can reduce the required curing time to an acceptable level. In fact, by utilizing high temperature and high shear, along with extended curing time, the rubber particles can be devulcanized and depolymerized into the asphalt to produce an asphalt-rubber binder that is both homogeneous and truly elastic. This can be done with no trade off in binder properties, in fact binder performance may be enhanced.

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## DISCLAIMER

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**Table 1. Experimental Plans (EPs)**

EP	Asphalt	Rubber Source	Mesh Size	Weight Percent	Mixer Speed	Temperature (°C)
#1	#1	Rouse	-10	10	500	191
		Tire Gator	-10, -40	5, 10		
	#2	Rouse	-10, -40, -80	5, 10		
		Tire Gator	-10, -40	10		
	#3	Rouse	-40, -80	5, 10		
		Tire Gator	-10	5, 10		
#2	#1	Rouse	-10	10	500, 1550	191
	#2	Tire Gator	-40	10		
#3	#1	Tire Gator	-40	10	500	177, 191, 204

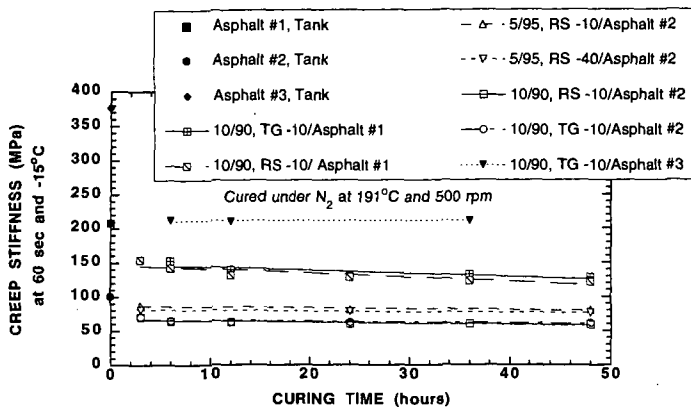


Figure 1. Low-Temperature Data

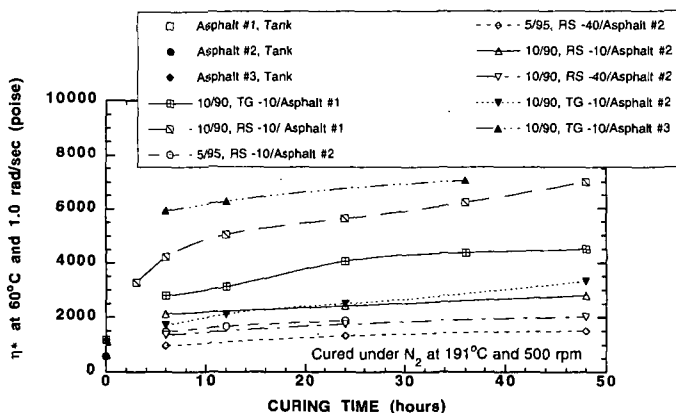


Figure 2. Intermediate-Temperature Data, Complex Viscosity

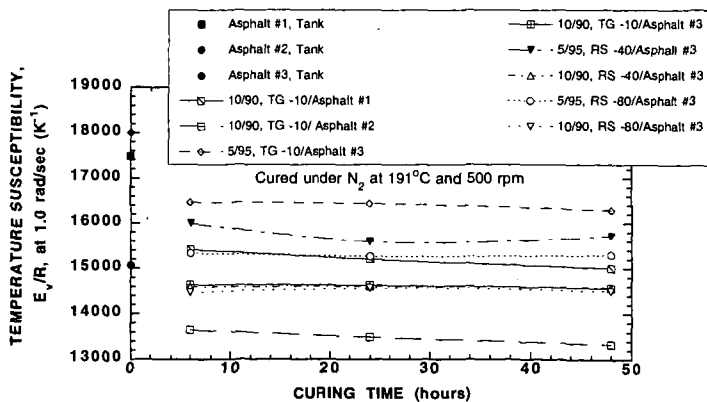


Figure 3. Intermediate-Temperature Data, Temperature Susceptibility

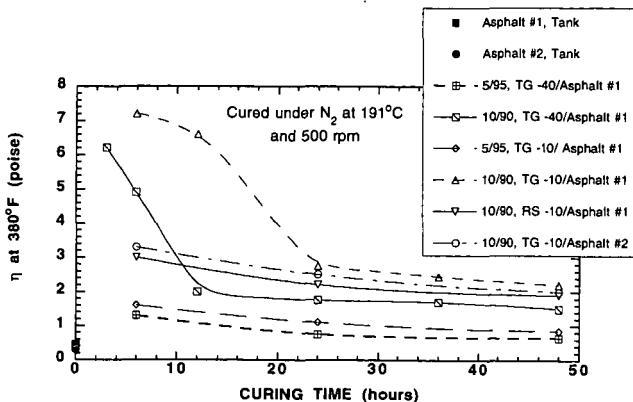


Figure 4. High-Temperature Data

### 10/90, RS -10/ASPHALT #1

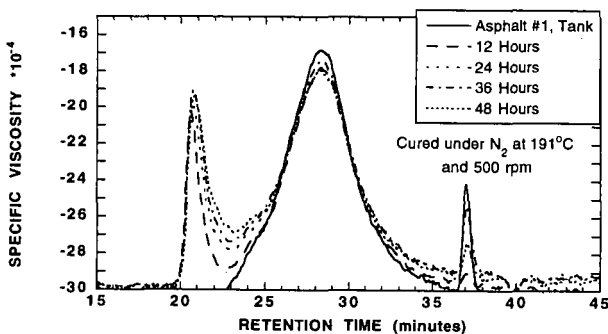


Figure 5. GPC Data for Asphalt #1

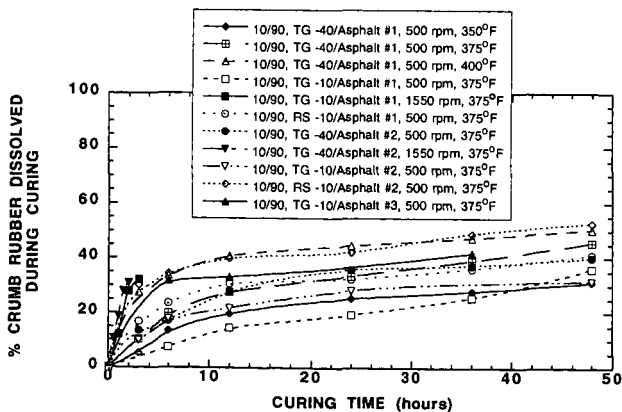


Figure 6. Rubber Dissolution Data